Temporary Entanglement Networks in Polymer Melts and their Effect on Rheological Properties

- A Molecular Dynamics Study $-^1$

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Abstract

The concept of mutual chain entanglements and temporary networks of entangled

chains has been very fruitful for quite a long time in understanding rheological and

viscoelastic properties of polymer melts. By analysing data from molecular dynamics

computer simulations entanglements can be detected in the melts. Structure and

dynamics of the entanglement networks can be assessed quantitatively. The results

can be correlated with the rheological properties of the systems which are extracted

simultaneously for stationary and nonstationary shear flows.

Key Words: Entanglements, Entanglement Network, Polymer Melts, Shear Flow

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1 Introduction

Computer simulations of polymer melts have provided a lot of interesting information about the relationship of rheology and structure in these systems [1, 2]. For a standard model (WCA+FENE bead spring model) the dependence of the zero shear rate viscosity on the molecular weight shows the cross over from Rouse ($\eta \sim M$) to entanglement regime ($\eta \sim M^{3.-3.4}$) [3]. This behaviour is an universal property of polymer melts which has been found from rheological measurements for a lot of different polymers [4, 5]. It is the aim of this paper to demonstrate how properties of entanglements and their temporary networks can be analysed from simulation data. We study the start-up of shear flow of a polymer melt until a stionary flow is established. The rheological properties (viscosity, normal presure differences) are extracted and compared with different quantities describing the entanglements in the system.

2 Simulation Method

The method of molecular dynamics computer simulations is a well established means for studying simple and complex fluids in equilibrium and nonequilibrium [6, 7]. The WCA+FENE bead-spring model of polymer melts used here has been described in detail elsewhere [1, 2, 3]. In the following we will use reduced units derived from the WCA-potential [6]. We choose a density of $\rho=0.84$ and a temperature of T=1. Our system consists of 100 chains with N=240 monomers each. The change of the molecular weight dependence of the zero-shear-rate viscosity occurs at $N\approx 100$

[2, 3]. The shear flow is imposed by a homogeneous shear algorithm [7, 6]. From the extracted pressure tensor the shear viscosity can be calculated via $\eta = -\frac{P_{xy} + P_{yx}}{2\gamma}$ with the shear rate γ .

The simulations were performed on a CRAY T3D parallel computer. The time step was chosen as $\Delta t = 5 \cdot 10^{-4}$. The calculations for one time step for 24000 beads took about 0.03s on 64 PEs.

3 Entanglements and Entanglement Networks

3.1 Entanglements

The mutual chain entanglement in polymer melts should be of great importance for the macroscopic properties of these materials [8, 9]. In the following we introduce a mathematical formulation of a criterion for chain entanglements based on the picture mentioned, i.e. it is a definition based on the configuration of chains in space [10, 11]. Then we will show that some first hand expectations on the special behaviour of entangled (parts of) chains can be fulfilled by the employment of this definition.

For simplicity in notation we consider polymer chains to be continuous curves $\underline{r}(\sigma)$ in space, parametrized by $0 \le \sigma \le 1$. A section of a chain A, $\{\underline{r}_A(\sigma)|\sigma \in I_A\}$, $I_A \subseteq [0,1]$, will be denoted as I_A . By connecting each point \underline{r}_A on a section I_A of a specific polymer chain A with all other points of this section, a convex volume

$$\mathcal{M}_{A}(I_{A}) = \bigcup_{\sigma_{1}, \sigma_{2} \in I_{A}} \left\{ \underline{r}_{c} \, \middle| \, \underline{r}_{c} = (1 - \lambda) \, \underline{r}_{A}(\sigma_{1}) + \lambda \, \underline{r}_{A}(\sigma_{2}) \,, \, \lambda \in (0, 1) \right\} \tag{1}$$

is constructed. It might reduce in the case of planar or straight curves to an area or a straight line. Intersections of sections of (other or the same) polymer chains with this volume \mathcal{M}_A will be called entanglements under the following conditions:

E1 Given two chains A and B and their corresponding volumes $\mathcal{M}_A(0,1)$ and $\mathcal{M}_B(0,1)$. Chains A and B are defined to be entangled in the points $\underline{r}_A(\sigma_e)$ and $\underline{r}_B(\tau_e)$ (short notation: $A \bowtie B \Big|_{\underline{r}_a(\sigma_e),\underline{r}_B(\tau_e)}$):

$$A \bowtie B \Big|_{\underline{r}_{A}(\sigma_{e}),\underline{r}_{B}(\tau_{e})} : \Leftrightarrow \bigvee_{0 \leq \sigma_{l} < \sigma_{h} \leq 1} \bigvee_{0 \leq \tau_{l} < \tau_{h} \leq 1} \bigvee_{\lambda, \mu \in (0,1)} \bigvee_{\underline{r}_{B}(\tau_{e}) = (1 - \lambda) \underline{r}_{A}(\sigma_{l}) + \lambda \underline{r}_{A}(\sigma_{h})}$$

$$\wedge \underline{r}_{A}(\sigma_{e}) = (1 - \mu) \underline{r}_{B}(\tau_{l}) + \mu \underline{r}_{B}(\tau_{h})$$

$$\wedge \tau_{e} \in (\tau_{l}, \tau_{h}) \wedge \sigma_{e} \in (\sigma_{l}, \sigma_{h}) . \tag{2}$$

E2 An entanglement is defined as a pair of chain sections $\{I_A, I_B\}$ fulfilling the following condition:

$$\bigwedge_{\sigma \in I_A} \bigwedge_{\tau \in I_B} \bigvee_{\mu \in I_B} \bigvee_{\nu \in I_A} A \bowtie B \Big|_{\underline{r}_A(\sigma),\underline{r}_B(\mu)} \wedge B \bowtie A \Big|_{\underline{r}_B(\tau),\underline{r}_A(\nu)}$$
(3)

It is useful for further definitions to introduce a characteristic function χ_{ij} for the entanglement of two chains i and j $\chi_{ij} = \begin{cases} 1, & i \bowtie j \\ 0, & \text{otherwise} \end{cases}$.

3.2 Numerics

For the numerical evaluation of the entanglement quantities the polymer system is mapped on a fine grid. Then the grid cells along the connecting lines \underline{r}_c spanning

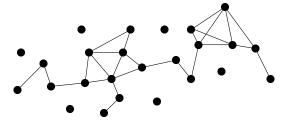


Fig. 1 Representation of a polymer melt; points denote chains, lines denote entanglements between chains at their ends.

the volume of, say, chain A, \mathcal{M}_A , are screened for intersections with other chains, e.g. $\underline{r}_B(\sigma_e)$. By checking if also chain A is intersecting \mathcal{M}_B near $\underline{r}_B(\sigma_e)$ the entangled points in the system are identified. When all entangled beads in the systems are found the chain sections corresponding to the entanglements can be constructed. The entanglement analysis is very time expensive. It takes for a system of $N_T = 24000$ and N = 240 about 120 s on a CRAY T3D using 32 PEs.

3.3 Entanglement Networks

Every definition of an entanglement which yields a characteristic function χ_{ij} can be used to describe the entanglement network. In the following we will use the concept introduced above. If we represent a polymer system by a number of points in space (e.g. for the centers of mass) the network can be sketched by lines between the points corresponding to entangled chains (fig. 1). The most simple characterization of the network is given by the average number of 'arms' of each point. We call this the network number ν . The network number roughly scales with the molecular weight like $\nu \sim N^{.5}$. For the network number a critical value $\nu_c \approx 23$ can be derived

for the case that all chains are entangled with their neighbours. For N=100 when the dependence of the zero shear rate viscosity on the molecular weight changes from the Rouse- to the entanglement-regime we find $\nu(N=100)\approx 23$. For a more detailed description of the entanglement network first the characteristic function χ_{ij} is generalized for the case of n chains. A n-plet of pairwise mutually entangled chains $\{i_1,\ldots,i_n\}$, i.e. $\chi^{(n)}_{i_1,\ldots,i_n}=1$ will be called a (pure) n-mesh or mesh of order In figure 1 simple entanglements (2-meshes) are represented by line, a 3-mesh is represented by a triangle, a 4-mesh by a tetrahedron and so on. The number of n-meshes in a system normalized by the number of chains will be denoted by $N^{(n)}$, $N^{(n)} = \frac{1}{N_k} \sum_{i, < i}^{N_k} \chi^{(n)}_{i_1, ..., i_n}$. 2-, 3- and 4-meshes span the entanglement network in 1, 2 and 3 dimensions and can therefore be regarded as primary meshes. Besides pure n-meshes where all n chains are pairwise mutually entangled of course there exist chain complexes as sketched in fig. 1. They are called general n-meshes where n is the highest order of a pure mesh comprised by this complex (fig. reff1 shows a 4-mesh). Of course, with increasing chain length the network number ν and the order of meshes present increase. While the $N^{(n)}$ characterize the static network structure the dynamics of individual meshes can be described by the following time correlation functions:

$$\mathbf{M}^{(n)}(t) := \frac{1}{N_k} \left\langle \sum_{i_1 < \dots < i_n}^{N_k} \chi_{i_1, \dots, i_n}^{(n)}(0) \chi_{i_1, \dots, i_n}^{(n)}(t) \right\rangle$$
(4)

The relative decay of different order meshes is described by ratios of the logarithmic derivatives $\frac{d}{dt} \log M^{(n)}$. Though for the decay of the entanglement network a complex evolution of the number ratios might be expected one can derive simple results under the assumption that all entanglements of a n-mesh decay with the same probability.

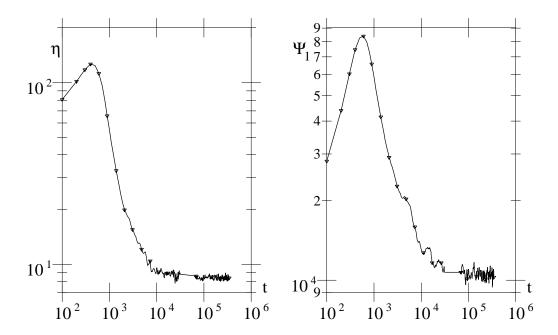


Fig. 2 Shear viscosity η (left) and first normal stress coefficient ψ_1 (right) as functions of time for the start-up of shear flow.

One finds $\frac{d}{dt}\log M^{(4)}=6\frac{d}{dt}\log M^{(2)}$, $\frac{d}{dt}\log M^{(3)}=3\frac{d}{dt}\log M^{(2)}$, $\frac{d}{dt}\log M^{(4)}=2\frac{d}{dt}\log M^{(3)}$. Deviations from this behaviour can easily detected by calculation of functions like $\Delta M42:=\log M^{(4)}-6\log M^{(2)}$.

4 Results

In this section we will present data from the simulation of a start-up of shear flow well into a stationary flow regime. We first show results for rheological properties. The shear viscosity (fig. 2) shows a clear stress overshoot. After about $t_v = 50000$ the viscosity becomes stationary. First and second normal stress coefficients $\psi_1 = \frac{P_{22}-P_{11}}{\gamma^2}$, $\psi_2 = \frac{P_{33}-P_{22}}{\gamma^2}$ show a similar behaviour (fig. 2) with similar relaxation times. From the concept of entanglements it can be expected that intermolecular as well

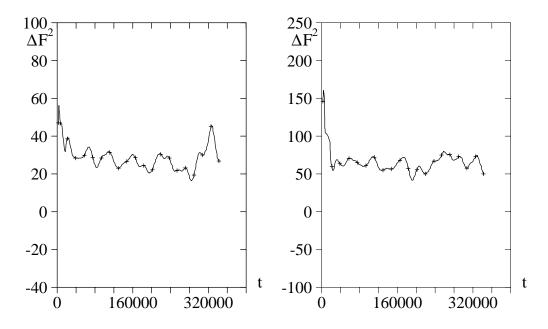


Fig. 3 Differences in the squared bonding (left) and intermolecular (right) forces between entangled chain sections and the system averages, $\Delta F^2 = \langle \ldots \rangle_E - \langle \ldots \rangle$.

as bonding forces in the system should be enhanced for entangled chain sections. This can be demonstrated by plotting the differences $\Delta F^2 = \langle F^2 \rangle_E - \langle F^2 \rangle$ for the intermolecular WCA- and the FENE-forces on the monomers (fig. 3). Indeed we find for the total time of our simulation a positive sign for this difference. The relaxation of the entanglement structure can be studied by the number of entanglements or by the network number ν (fig. 4). We find in the stationary flow $\nu=45$. The ratios $\frac{N^{(4)}}{N^{(3)}}$, $\frac{N^{(4)}}{N^{(2)}}$, and $\frac{N^{(3)}}{N^{(2)}}$ indicate the relaxation of the entanglement structure into a stationary state after $t_r \approx 10^5$ (fig. 4). In the stationary flow regime the dynamics of the entanglement network can be studied by the time correlation functions $M^{(2)}(t)$, $M^{(3)}(t)$, and $M^{(2)}(t)$ (fig. 5). For times up to approximately the relaxation time t_r the decay seems to follow a power law; this corresponds to a broad distribution of decay

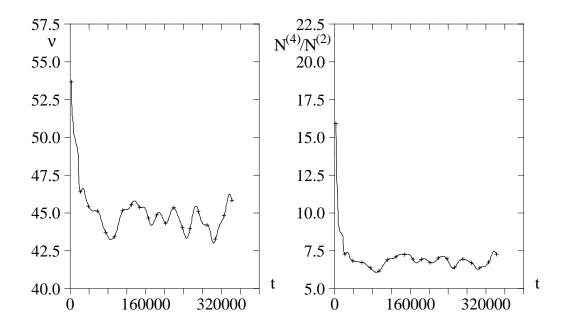


Fig. 4 Relaxation of the network number ν (left) and the ratios of mesh numbers: $N^{(4)}/N^{(2)}$ during the nonstationary flow phase (right figure).

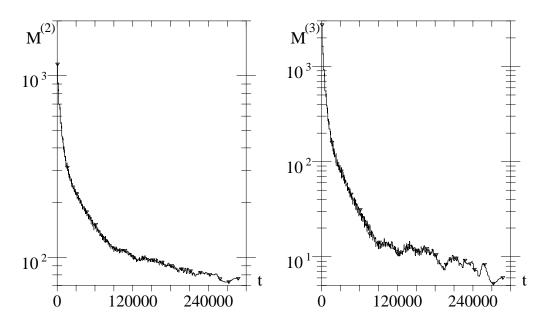


Fig. 5 Decay of the time correlation functions for the low order meshes in the stationary flow regime, M⁽²⁾ (left) and M⁽³⁾ (right).

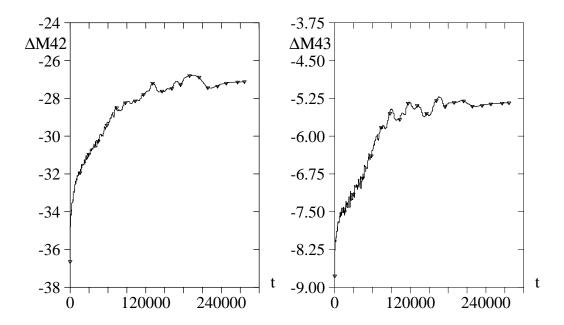


Fig. 6 Comparison of the decay of the time correlation functions for the low order meshes in the stationary flow regime. $\Delta M42 = \log M^{(4)}(t) - 6 \log M^{(2)}(t)$ (left) and $\Delta M43 = \log M^{(4)}(t) - 2 \log M^{(3)}(t)$ (right).

times of entanglements. For longer times the time correlations can be fitted by an exponential decay. The differences $\log M^{(4)}(t) - 6 \log M^{(2)}(t)$, ... increase rapidly for $t < t_r$ indicating a much faster decay of lower order meshes (fig. 6). For times longer than t_r they grow slowly; for these times they describe a slow decay of meshes in the entanglement network which might be called metastable. Due to the finite system size and the periodic boundary conditions used the extracted $M^{(n)}(t)$ may decay only to a constant noise value > 0. However, a stationary value is not observed during the time of our simulations!

5 Conclusions

We presented rheological data and results for the entanglements in a polymer melt in nonstationary and stationary shear flow. While the rheological data suggest a relaxation time into the stationary flow regime of about $10^4 - 5 \cdot 10^4$ we find longer total decay times for the entanglement network. This has an encouraging consequence for the simulation of shear flows with very low shear rates (determination of zero shear rate viscosity) if the relaxation of the rheological properties is faster than that of the network structure. The different decay times for different order meshes of the entanglement network are examples of multiple-chain effects in the dynamics of polymer melts; the disentanglement time of two chains depends on their involvement in entanglements with other chains. As a result of the long decay times for some entanglements one might consider the system as effectively polydisperse if always a certain number of molecules is involved in long living complexes of two and more entangled chains. It seems promising to continue the work presented here into different directions. On one hand it is an interesting question how the entanglement dynamics depend on the chain length? Do other critical chain lengths exist like the entanglement length $N \approx 100$ (where the entanglement network becomes continously connected, $\nu \approx 23$)? On the other hand the network dynamics for different shear rates is of interest. How do decay times (and their distributions) change for higher shear rates; become at least some meshes stabilized (like knots under tension) or will they be resolved more quickly due to higher forces? And for very low shear rates: do chain complexes really influence the diffusion along the chain (or tube) contour described by the reptation model?

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